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In situ measurement of mechanical property and stress evolution in a composite silicon electrode

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HIGHLIGHTS

- Large curvature change of a Si/PVDF composite electrode is observed during cycling.
- A method is proposed to measure elastic modulus and stress in the electrode.
- Effect of crack formation on stress evolution and mechanical behavior is revealed.

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ABSTRACT

Mechanical properties and lithiation-induced stress are crucial to the performance and durability of lithium-ion batteries. Here, we report the evolution of elastic modulus and stress in a silicon/polyvinylidene fluoride (PVDF) composite electrode coated on a copper foil, along with a model for analyzing the large change in the radius of curvature of the composite electrode/copper foil cantilever. The radius of curvature of the cantilever is captured by a video camera during lithiation/delithiation. The elastic modulus of the composite electrode decreases from about 0.64 GPa to 0.18 GPa during lithiation. It decreases further to about 0.10 GPa after delithiation, which is caused by the fracture of the electrode. The magnitude of the compressive stress increases lineally during lithiation and decreases suddenly to reach a steady state value during delithiation.

1. Introduction

Stress effects on the performance and durability of lithium-ion batteries (LIBs) have been widely investigated [1–3] to help develop the next generation of LIBs with higher energy density, longer cycle life, and faster rate capabilities. Specifically, silicon (Si) is one of the most promising negative electrode materials because of its high theoretical capacity (~3600 mAhg^{-1}). However, compared with commercially used graphite electrodes, Si experiences much larger volumetric expansion upon fully lithiation (~12% for graphite; 300% for Si) which can cause significant stress [4], leading to cracking and delamination. Hence, observing stress evolution and measuring changes in mechanical properties of Si-based electrodes during electrochemical cycling are crucial for understanding and enabling these electrodes for future LIB applications.

Several *in situ* measurements of the changes in structure, composition, and morphology of the electrodes have been reported in the literature, including transmission electron microscopy [5], x-ray transmission microscopy [6], atomic-force microscopy (AFM) [7,8], nuclear magnetic resonance (NMR) [9] and optical stress sensors. Usually, *in situ* measurements were conducted in thin film electrodes. For example, Dahn and co-workers [10,11] used *in situ* optical microscopy and AFM to study deformation in Li-alloy thin film electrodes and revealed that cracks appeared primarily due to

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the lateral contraction of the films during the delithiation process. Stress evolution of thin film electrodes has been monitored by the *in situ* wafer-curvature technique [12–16]. It measures the change in the curvature of the inactive and stiff substrate and then converted it to an in-plane stress in the film using Stoney's equation [17]. In additional to measuring stress, Sethuraman et al. [13–15] completed a series of wafer-curvature experiments to monitor the changes in thin film electrode properties, such as biaxial modulus and stress-potential coupling, during electrochemical cycling. The same technique was also used to obtain real-time stress measurements on carbon thin film electrodes and the stress at the substrate/current collector was about 0.25 GPa [12]. These studies provide insights into the mechanisms associated with deformation and stress development in LIB electrodes.

The mechanical properties of LIB electrodes have also been calculated by *ab initio* quantum mechanics. Qi et al. [18] studied the Young's modulus of graphite electrodes during lithium intercalation using the Density Functional Theory and found that the polycrystalline Young's modulus of graphite electrode tripled as it was lithiated to LiC_6. Yang et al. [19] calculated that the Young's modulus of Li_xSi would decrease from 160 to 40 GPa with increasing Li content in the alloy. However, the *in situ* experimental measurement of mechanical properties such as elastic modulus is much needed.

Composite electrodes, which are typical in commercial LIBs, have a complex porous structure consisting of active particles, conductive graphite, and polymeric binders. It is difficult to measure *in situ* mechanical properties and stress evolution in composite electrodes during electrochemical cycling. The objective of this work is to measure *in situ* the elastic modulus and stress evolution in a composite Si/PVDF electrode. A cell made of quartz was constructed for *in situ* measurements of the curvature change of the composite electrode and a mathematical model was developed to analyze the evolution of curvature, modulus, and stress in the composite electrode during electrochemical cycling.

2. Experiment

2.1. Electrode preparation and cell assembly

Composite Si electrodes were made by mixing 50 wt% Si powder (size 30–50 nm, Nanostructured & Amorphous Materials), 25 wt% conductive carbon black (Super P C65, TIMCAL), and 25 wt% PVDF binder (Alfa Aesar) to form a slurry [20]. The N-methyl-2-pyrrolidone (NMP, 99.5%, Alfa Aesar) was used as the solvent to dissolve PVDF (weight ratio of 36.3:1). Then, the slurry was casted onto a battery grade Cu foil (24 μm thick) by using a 127 μm gap doctor blade. The electrodes were dried at 130 °C for 12 h in a vacuum oven. A calendering machine (MIT Corporation) was used to press the electrode to a porosity of 32.5% (see Table 1 and Appendix).

A layered electrode configuration shown in Fig. 1 was used to investigate the relationship between curvature (κ) and the state of charge (SOC) in the electrochemical experiments. The electrochemical cell is made of transparent quartz which allows the measurement of the deformation of the layered electrode by a video camera (JAI). A porous 12 μm thick Si/PVDF composite electrode deposited on a 24 μm thick copper foil served as the working electrode, while a lithium metal (3 mm thick, 60 mm length and 4 mm width, Sigma Aldrich) was used as both a reference and counter electrode. The two electrodes, in the form of two cantilever beams, were positioned facing each other and separated by a piece of microporous polypropylene film (Woven Celgard C3501 separator of thickness 21 μm, Celgard, Inc.). The cell was filled with 1 M $LiPF_6$ salt in a mixture of ethylene carbonate and diethyl carbonate (EC: DEC = 1:1 vol%, BASF). The experiment was done in a glove-box filled with ultra-high purity argon.

Table 1
The volume fraction of each composition.

	Mass (mg)	Density (g/cm^3)	Volume (cm^3)	Volume fraction
Si	0.8920.357	2.329	0.000153	28.3%
CB	0.1785	1.6	0.000112	20.5%
PVDF	0.1785	1.77	0.000101	18.7%
Porosity	–	–	–	32.5%

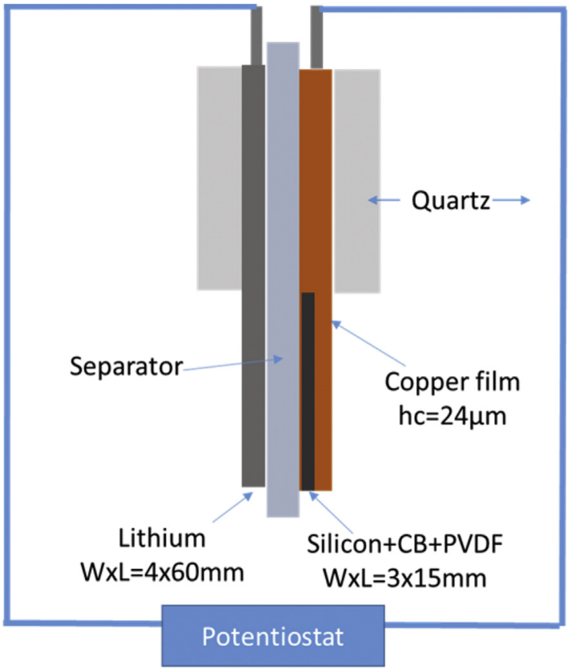

Fig. 1. A schematic illustration of the electrochemical cell.

2.2. Electrochemical test

Electrochemical cycling of the composite Si electrode was carried out in the cell described above at room temperature using BioLogic potentiostats (MPG-2 and VMP-3, BioLogic). The cell was cycled galvanostatically at a current density of 142.1 μA/cm^2 (ca.$C/20$C-rate, theoretical capacity of 3600 mAhg^{-1} for silicon) for 6 h, followed by an open-circuit potential relaxation for 4 min between 0.01 and 2V *vs.* Li/Li$^+$. A charge-coupled video camera (JAI) was used to acquire pictures of the electrode during electrochemical cycling. Fig. 2 shows the change in the curvature of the composite electrode during lithiation.

2.3. Mathematical model of curvature change

Mechanical analysis provides an insight into the mechanism of deformation process. Fig. 3a illustrates the bilayer electrode geometry in the experiments by bonding an active layer to a current collector to form a cantilever. Here, h_1 and h_c denote the thickness of the active layer and current collector, respectively. The composite electrode expands and contracts as lithium diffuses into and out of the active layer during electrochemical cycling. As the active layer expands (contracts) while the current collector restricts it, the composite electrode will bend to a larger (smaller) curvature, as shown in Fig. 3b. Let the thickness direction be aligned with the z-axis and the plate is in the x-y plane. Lithium ions are allowed to be